

CHAPTER II

LITERATURE REVIEW



2.1 General

Cement production is an extremely energy-intensive process. The average energy requirement to produce 1 ton of cement is approximately 4.4 million Btu (Ullman, 1991). This amount of energy is roughly equivalent to 400 pounds of coal. Because of the vast energy requirements, the cement industry is continually investigating more economical production technologies and fuel options. In the 1970s, the U.S. cement industry recognized that hazardous waste with a high energy and low chlorine content could be used as a fuel in cement kilns (Costner and Thornton, 1990). This idea is continually needed to manage hazardous waste. At present, one of more controversial options in waste management is the burning of hazardous waste in cement kilns. The most significant benefits are recovery of the energy value from the hazardous waste, conservation of nonrenewable fossil fuels, and reduction in a facility's fuel costs. Regardless of these benefits, several issues must be considered. The most important of the utilization of hazardous waste as a fuel in the cement industry is that it can burn hazardous waste safely and it does not adversely affect human health.

2.2 Cement production process

In general, there are 3 processes to produce cement which are wet process, semidry process, and dry process (Peray, 1986).

In the wet process, the raw material is blended with water to raise homogenization of the mixture. The resulting slurry, which is typically 30 to 40% water, is fed directly into the kiln. In comparison with a dry process kiln of the same diameter, a wet process kiln needs an additional zone (dehydration zone) to remove

the water from the raw material. To produce an equivalent amount of clinker, a wet process kiln requires more fuel than a dry process kiln because of the extra heat required to evaporate the water. However, in actual operation of a kiln this fundamental fact does not always hold entirely true. The advantages of a wet process are:

- Feed is blended more uniformly than in the dry process
- Dust losses are usually smaller.
- In moist climate regions, wet processing of the raw material is more suitable than dry because of moisture already present in the blend materials.

In the semidry process, water typically 10 to 15% is added to the ground dry feed material. The pellets that result are loaded onto a traveling grate through which the cement kiln's hot exit gases are drawn. By the time the feed material reaches the kiln entrance, the water has evaporated and calcination has begun. Since the hot exit gases of the kiln are used to dry, preheat, and initiate calcination of the feed material, the semidry process is extremely energy efficient.

In the dry process, the raw material enters the kiln in a dry powdered form. This process is characterized by three types of cement kilns which are the dry kiln, the preheater kiln, and the precalciner kiln. The oldest type is known simply as the dry kiln. The preheater kiln became popular after World War II. This type of kiln is equipped with a tower of heat-exchanging cyclones in which the raw material is preheated and partially calcined by the kiln's exit gases prior to entering the actual kiln. Because of the buildup of volatile components such as alkali salts, sulfur and chlorides in the lower cyclone stages and kiln entrance, the preheater kiln must be equipped with a bypass to divert a portion of the kiln's hot exit gases from the tower to air pollution control devices. The precalciner kiln represents the most recent technological advancements. The precalciner kiln is identical to the preheater kiln except that a secondary firing device is added to the lower stage of the preheater tower in which further calcination of the material occurs. Consequently, the majority of the material that enters the kiln is completely calcined. The cement product process is shown in the figure 2.1

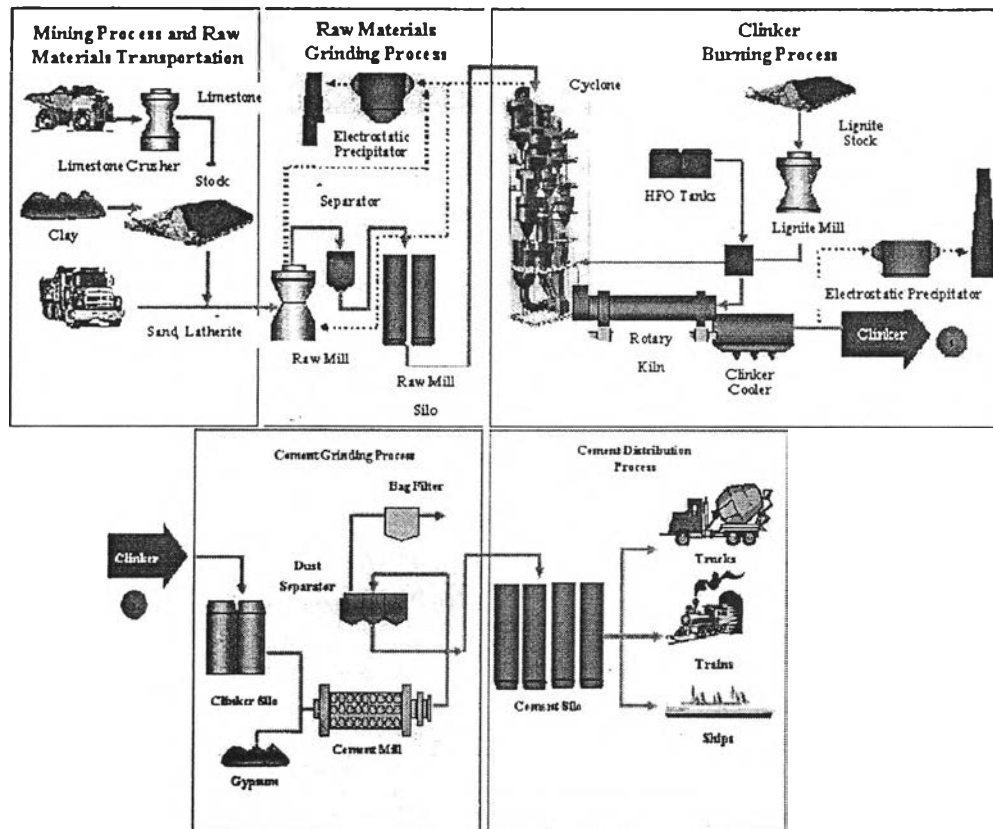


Figure 2.1 Cement production process (Karl and Richter, 2004)

2.3 Kiln system chemistry

Cement manufacturing consists of raw meal grinding, blending, pre-calcining, clinkering, burning and cement grinding. The chemical reactions occur at pre-calcining, and burning processes. The most important oxides that participate in the reactions are CaO , SiO_2 , Al_2O_3 and Fe_2O_3 . This raw meal is blended and sent to a rotary kiln. The temperature is increased when transported from the meal feed to the rotary kiln. First, water is removed from raw material when the temperature is higher than 100°C . Then, the temperature is reached to the range of $700\text{--}900^\circ\text{C}$, which is called calcining zone. In this zone, calcium carbonate is changed to calcium oxide and carbon dioxide. After that, the temperature is increased to the range of $900\text{--}1,200^\circ\text{C}$. In this zone, calcium oxide reacts with silica dioxide to produce dicalcium silicate (C_2S). Then, calcium oxide reacts with dicalcium silicate to produce tricalcium silicate (C_3S). Tricalcium silicate occurs at the temperature range $1,250\text{--}1,450^\circ\text{C}$. After that, the temperature is decreased very quickly to prevent decomposition of

tricalcium silicate. During the cooling step, tricalcium aluminate and tetracalcium aluminoferrite is formed. The chemical reactions of each step are shown in the equation below. After that, the clinker was ground and homogenous mixed with gypsum. The product is called cement (Alsop, 1998).



2.4 Raw Materials

The production of cement requires the following components: calcium carbonate (CaCO_3), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). Limestone typically provides the calcium carbonate. Clay or shale provides the remaining components. The typical component of some raw materials is shown in the Table 2.1.

Table 2.1 Typical composition (% weight) of some raw materials

Component	Limestone	Marl	Clay	Sand	Bauxite	Iron ore
LOI	40.38	24.68	7.19	0.2	15-20	5-12
SiO_2	3.76	27.98	67.29	99.2	16-22	20-25
Al_2O_3	1.10	10.87	8.97	-	44-58	3-9
Fe_2O_3	0.66	3.08	4.28	0.5	10-16	45-60
CaO	52.46	30.12	7.27	-	2-4	0.5-2.5
MgO	1.23	1.95	1.97	-	0.2-1.0	1.5-7
K_2O	0.18	0.20	1.20	-	-	0.3-0.6
Na_2O	0.22	0.33	1.51	-	-	-
SO_3	0.01	0.70	0.32	-	-	-
Total	100.0	99.91	100	99.9	-	-

The raw materials used in the cement production process naturally contain metals and halogens. Thus, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, vanadium, zinc, bromine, chlorine, fluorine, and iodine are typically present in the raw materials. The amounts of these components depend on the geological formations from which the raw materials are mined.

2.5 Chemical compounds of cement clinker

The raw materials used in the manufacture of Portland cement consist mainly of lime, silica, alumina and iron oxide. These compounds interact with one another in the kiln to form a series of more complex products and, apart from a small residue of uncombined lime which has not had sufficient time to react, a state of chemical equilibrium is reached. However, equilibrium is not maintained during cooling, and the rate of cooling will affect the degree of crystallization and the amount of amorphous material present in the cooled clinker. Four major compounds of cement are listed in table 2.2.

Table 2.2 Major compounds of Portland cement (Taylor, 1990)

Name of compound	Oxide composition	Abbreviation
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S (alite)
Dicalcium silicate	$2\text{CaO} \cdot \text{SiO}_2$	C_2S (belite)
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A (aluminite)
Tetracalcium aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF (ferrite)

The calculation of the potential composition of Portland cement is based on the work of R.H. Bogue and others, and is often referred to as "Bogue composition". Bogue's equations for the percentages of main compounds in cement are given below (Bernal et.al., 1952).

$$C_3S = 4.07(\text{CaO}) - 7.60(\text{SiO}_2) - 6.72(\text{Al}_2\text{O}_3) - 1.43(\text{Fe}_2\text{O}_3) - 2.85(\text{SO}_3) \quad (2.6)$$

$$C_2S = 2.87(\text{SiO}_2) - 0.75(3\text{CaO} \cdot \text{SiO}_2) \quad (2.7)$$

$$C_3A = 2.65(\text{Al}_2\text{O}_3) - 1.69(\text{Fe}_2\text{O}_3) \quad (2.8)$$

$$C_4AF = 3.04(\text{Fe}_2\text{O}_3) \quad (2.9)$$

Estimating the composition of cement is aided by more rapid methods of determining the elemental composition, such as X-ray fluorescence, X-ray diffraction spectrometer, atomic absorption, flame photometry, and electron probe micro-analysis. X-ray diffractometry is useful in the determination of free lime.

Tricalcium silicate, which is called alite, is an important composition as it is responsible mainly for early strength development of mortar and concrete. C_3S is a highly hydraulic compound occurs in amounts of 50-90% in Portland cements. C_3S is formed above 1250°C by a reaction of C_2S and CaO and can be metastably obtained by rapid cooling of the mixtures. The crystalline structural model is given in Figure 2.2 (a).

Dicalcium silicate, which is called belite, mainly occurs in an amount of 10-40% in the clinker. C_2S is capable of incorporating larger amounts of foreign ions than C_3S . Activated C_2S can be obtained by rapid cooling, lattice distortions by solid solutions, crystal size, crystallochemical changes and chemical shift of bonding energies. The structural model of C_2S is shown in Figure 2.2 (b).

Tricalcium aluminate, which is called aluminite, is responsible for the workability of the mortar. The higher the C_3A content, the higher the plasticity of the mortar. This explains why raw material for plastic cements has a higher C_3A potential than typical cement. The C_3A has 6-8% of the clinker. Concrete containing cement high in C_3A is not as resistant to attack by sulfates in soil or water exposure as is concrete made with low C_3A cement. The structural model of C_3A is shown in Figure 2.2 (c).

Tetracalcium aluminoferrite, which is called ferrite, governs the color of the cement. The higher the content of C_4AF in the clinker causes the darker the cement. Iron has the desirable property of acting as a fluxing agent in the kiln, facilitating formation of other compounds of the cement at somewhat lower temperature than would otherwise be possible. The structural model of C_4AF is shown in Figure 2.2 (d) (Bensted and Barnes, 2002; Brown, 1948).

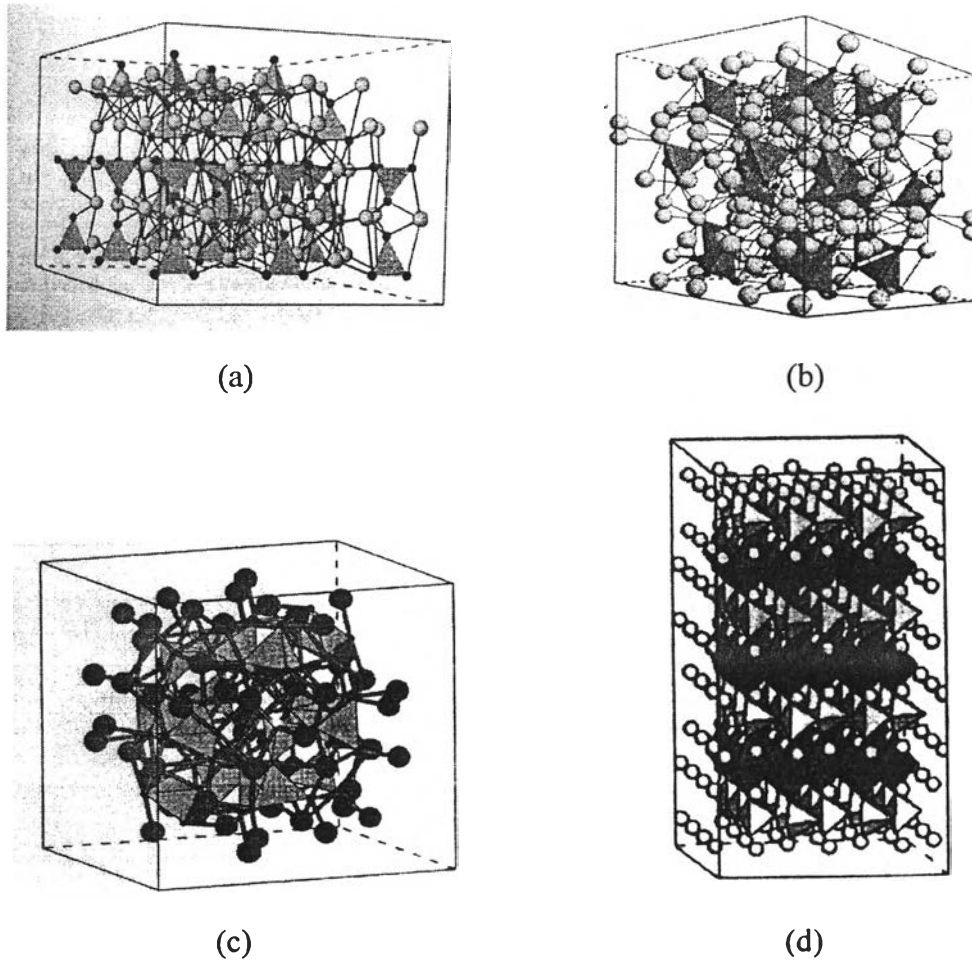


Figure 2.2 Structure model of major components of clinker: (a) C_3S (b) C_2S (c) C_3A (d) C_4AF (Bensted and Barnes, 2002)

2.6 Hazardous waste as a supplemental fuel and raw material

Typically, a cement kiln is fired with coal, petroleum coke, oil, or natural gas. However, some cement production facilities have used hazardous waste to replace a portion of their conventional fuel and raw material. Burning hazardous waste in cement production process is not only disposing hazardous waste, but also recover energy from the waste. Normally, the waste that disposed in cement kiln consisted of used oil, solvent, tires, waste wood, and sludge from waste water treatment plant. Examples of the waste are shown in Figure 2.3 and Table 2.3. These waste consisted of heavy metal such as lead in used oil and solvent, cobalt and cadmium in plastic, chromium and nickel in sludge and zinc in old tires.

The hazardous waste does not have energy value and the composition of them similar to raw material of cement such as SiO_2 , Al_2O_3 and Fe_2O_3 . It has used as alternative raw material. For the waste to serve as a suitable supplemental fuel, it must be combustible and have significant energy content. The advantages of the use of hazardous waste as alternative fuel or alternative raw material are following:

- Conservation of nonrenewable fossil fuels
- Reduction in production costs
- Use existing technology to treat large volumes of hazardous waste
- Waste treatment does not require any addition source of heat
- There is no increase in discharges to the atmosphere.

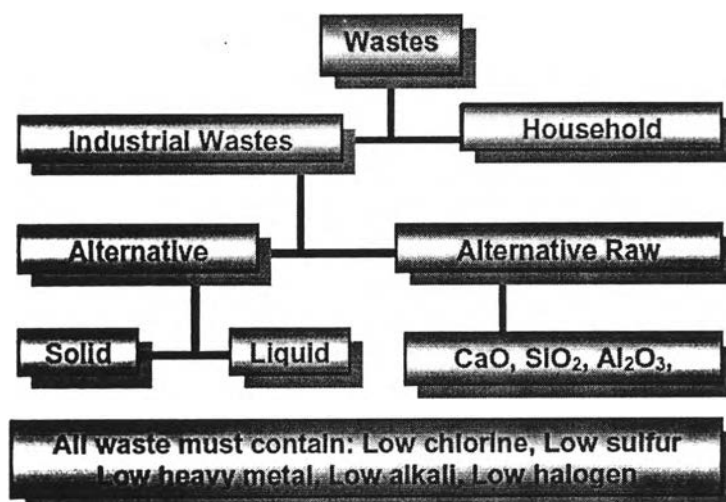


Figure 2.3 Examples of the waste dispose in cement kiln

Table 2.3 Examples of waste used as alternative raw material and alternative fuel

Alternative raw material	Alternative fuel
Wastewater sludge	Used oil, solvent and thinner
Adsorbent	Paint sludge
Ashes	Oil-contaminated cotton/Glove
Slag	Spent charcoal, activated carbon and wax
Iron power	Resin
Silica rich material	Plastic, old tires and wood
Etc.	Etc.

2.7 Classification of alternative fuel and alternative raw material

Alternative fuels are the solid, liquid, municipal or industrial wastes used in industrial and power plants as a substitute for conventional fuels. Alternative fuels have been in use for more than 10 years. Alternative fuels used in the cement industry are usually classified according to the concentration criterion into 3 groups (Jenkins and Mather, 1997; Pizant and Gauthier, 1997):

- Gaseous (i.e. landfill gas, pyrolysis gas)
- Liquid (i.e. pasty wastes, solvents, waste oils, greases)
- Solid (i.e. animal powder, bark, paper, tires, rubber wastes, plastics, fluff)

According to the classification by the Cembureau, alternative fuels are classified into 5 types that are following (Cembureau, 1999):

- Class 1: Gaseous alternative fuels (i.e. refinery waste gas, landfill gas)
- Class 2: Liquid alternative fuels (i.e. low chlorine spent solvents, hydraulic oil)
- Class 3: Pulverized, granulated or finely-crushed solid alternative fuels (i.e. sawdust, dried sewage sludge, granulated plastic, animal flours, fine crushed tires)
- Class 4: Coarse-crushed solid alternative fuels (i.e. crushed tires, rubber/plastic waste, wood waste, reagglomerated organic matter)
- Class 5: Lump alternative fuels (i.e. whole tires, plastic bales)

Solid alternative fuel may be classified into 4 groups (Paulin, 1998)

- Group 1: Solid, dry fuels of relative fine size, which do not adhere (dimensions : < 2 mm., humidity < 10-15%) i.e. wood dust, bark powder, rice husk
- Group 2: Solid, dry fuels of coarse size, which do not adhere (dimensions < 20 mm., humidity < 10-15%) i.e. plastic waste, wood chips, waste wood
- Group 3: Solid, dry fuels which tend to stick (dimensions < 20 mm., humidity < 10-15%) i.e. animal powder, impregnated wood dust
- Group 4: Mixtures of different lumpy fuels (dimensions < 200 mm., humidity < 20%) i.e. fluff, paper, cardboard

There is also another classification of solid and liquid fuels used in cement industries are separated into 3 types (Grosse-Daldrup and Scheubel, 1996).

- Type 1: Vegetable compounds or natural products (i.e. oil shale, peat, barks, sawdust, and etc.)
- Type 2: Synthetic products (i.e. used tires, rubbers waste, waste plastic, and etc.)
- Type 3: Others (i.e. parts of shredded cars, fuels derived from rejects, household garbage, and etc.)

Liquid fuels are separated into 2 types:

- Type 1: Liquid substitute fuels – easily decomposed, slightly toxic (i.e. acid tar, oil residues, and etc.)
- Type 2: Liquid substitute fuels, stable toxic (i.e. polyaromatic hydrocarbons (PAHs), polychlorinated biphenyl(PCB), and etc.)

The burning of various types of wastes requires the detailed control and adaptation of technological processes to each type of waste. For this reason, the properties of the waste should be analyzed to find the suitable proportion of the waste for the use. The following properties of the waste are described as follow (Cembureau, 1999; Greco, 1996):

- Physical state of the fuel (solid, liquid or gaseous)
- Content of circulating elements (Na, K, Cl or S)
- Toxicity (Organic compounds or inorganic compounds)

- Composition and content of ash
- Content volatiles
- Calorific value
- Physical properties (Scrap size, density, homogeneity)
- Grinding properties
- Humidity content
- Proportioning technology

2.8 Chromium, nickel, and zinc

2.8.1 Chromium

Chromium is an element found naturally in rocks, soil and plants. It occurs in combination with other elements as chromium salts, some of which are soluble in water. The pure metallic form rarely occurs naturally. Chromium does not evaporate, but it can be present in air as particles. In nature, it is found in three forms: metal ore, trivalent chromium (Cr III), and hexavalent chromium (Cr VI). Chemical properties of chromium are as follows (Vincoli, 1997):

Atomic weight:	51.996
Melting point:	1,857°C
Boiling point:	2,672°C
Density:	7.14 g/cm ³

In general, chromium (VI) is more toxic than chromium (III) because its oxidizing potential is high and it easily penetrates biological membranes. Chromium is a confirmed human carcinogen. It is a human poison by ingestion with gastrointestinal effects. It can also be toxic by inhalation. Exposure to the dusts of chromite and ferrochrome alloys may cause lung diseases, including pulmonary fibrosis and pneumoconiosis.

In cement industries, chromium is found in limestone, clay, char, and oil which are the fuel sources in production process (Sprung, 1985). Hazardous waste co-incineration in cement kilns uses waste as fuel or as raw material in partial substitution for natural materials. Waste such as galvanic sludge and electroplating sludge can be used in the co-incineration (Denise et.al., 2000).

2.8.2 Nickel

Nickel is a very abundant natural element. Pure nickel is a hard, silvery-white metal. Nickel can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. Nickel is found in all soil and is emitted from volcanoes. Nickel is also found in meteorites and on the ocean floor. Nickel and its compounds have no characteristic odor or taste. Chemical properties of nickel are as follows (Vincoli, 1997):

Atomic weight:	58.71
Melting point:	1,455°C
Boiling point:	2,730°C
Density:	8.9 g/cm ³ at 25°C

Nickel is a severe human poison by ingestion and inhalation of its finely divided powders and dusts. Skin contact with the dusts of nickel may result in scratching and scarring. Nickel is a confirmed carcinogen in animals causing lung and nasal tumors. Its carcinogenic potential in humans is considered highly suspect. Inhalation of nickel dusts or fumes can cause severe inflammation and irritation of the upper respiratory tract with nonproductive cough, rapid breathing, and tightness in the chest.

In cement industries, the main sources of nickel in production Portland cement are limestone, clay, coal, oil, and coke (Sprung, 1985). Waste such as galvanic sludge and electroplating sludge were disposed in cement process. These wastes are one of the main sources of nickel (Ract et.al., 2003).

2.8.3 Zinc

Zinc is an element commonly found in the earth's crust. In nature zinc occurs as a sulfide, oxide, or carbonate. In solution, it is divalent and can form hydrated Zn^{2+} cations in acid. Zinc ligands are soluble in neutral and acidic solution, so that zinc is readily transported in most natural waters, but zinc oxide, the compound most commonly used in industry, has a low solubility in most solvent. Zinc appears as a shining white metal with a bluish-white or gray luster. It is used in alloys, electroplating, metal spraying, and auto parts. Chemical properties of zinc are as follow (Vincoli, 1997):

Atomic weight:	65.37
Melting point:	419°C
Boiling point:	907°C
Density:	7.14 g/cm ³

Zinc exhibits relatively low toxicity, but its compounds and salts are highly toxic. It is primarily toxic through inhalation of its dusts. Zinc is poorly absorbed through the digestive tract and, therefore, ingestion is not considered a toxic exposure route. Skin contact may cause localized irritation. There are no data in the references regarding its carcinogenic or mutagenic properties. Inhalation of zinc dusts can lead to coughing, phlegm, sneezing, and other indications of mechanical irritation.

In cement industries, zinc is present as a minor element in tires. It is extensively used as alternative fuel in cement industry worldwide. It is also found in electroplating sludge (Suwimol and Duangruedee, 2004).

2.8.4 Heavy metals in cement

Normally, the cement industries have a guideline to receive the hazardous waste for disposing in the production process. Table 2.4 is the guideline of heavy metals in the waste that the cement industry can receive this waste to dispose in the production process.

Table 2.4 Acceptable range of heavy metals in hazardous waste for cement industry

Heavy metal	Concentration, wt. %
Arsenic	≤ 0.5
Barium	≤ 10.0
Cadmium	≤ 0.1
Chromium	≤ 0.5
Copper	≤ 4.0
lead	≤ 1.0
Mercury	≤ 0.05
Nickel	≤ 10.0
Silver	≤ 10.0
Selenium	≤ 10.0
Vanadium	≤ 10.0
Zinc	≤ 10.0

Although a metal compound is changed in the combustion process, it is not destroyed in a combustion device. Normally, heavy metals occur only in minor quantities in cement and do not cause any problem. The metals will be present in the emission, the cement kiln dust or the clinker. The recent studies have focused on the metals that might be present in the raw material or fuel involved in the cement production process. Sprung (1985) studied the behavior of arsenic, cadmium, chromium, lead, nickel, thallium, and zinc. Most of these metals fed into the raw material were retained in the clinker and cement kiln dust. The result indicated that the distribution of a metal between the clinker and the cement kiln dust depend on the quantity of the metal fed into the kiln, the chloride content, or the manufacturing process. For example, the distribution of zinc, arsenic, chromium and nickel was relatively insensitive to both the production process and the chloride content, and was largely bound in the clinker.

Stephan et al. (1999) studied the influence of high intakes of Cr, Ni and Zn on the burning process and the formation of the clinker phase. In this study, clinker was simulated in a laboratory. The results showed that only very high intakes of heavy

metals had a measurable effect on the formation and composition of the clinker. In addition, Barros et al. (2004) investigated the effects of Cr_2O_3 and NiO additions on transformations during the production of Portland cement clinker. The results showed that the Cr_2O_3 additions to cement raw meal act as an inhibitor C_2S formation. NiO has very little effect on clinker reactions but Ni does cause a small increase in the temperature of C_2S formation. Also, all the Ni added to the charge was not lost during processing.

Murat et al. (1996) examined the effects of large additions of Cd, Pb, Cr and Zn to Portland cement raw meal on the composition and properties of clinker. The results showed that a large amount of chromium (84%) was trapped and 53% of zinc was fixed in Portland cement clinker. Also, ZnO addition increased the alite size crystals.

von Seebach and Tompkins (1991) investigated the fate of metals in the cement kiln system. Three dry process cement kilns equipped with precalciners, two dry process cement kilns equipped with preheaters, and one wet process cement kiln was used in the investigation. The metals investigated were antimony, arsenic, barium, beryllium, cadmium, chromium, lead, nickel, selenium, silver, vanadium, and zinc. The total input and output of the metals were analyzed to estimate the retention in the process solids versus the concentrations in the emission. The results show that greater than 99% of the metals were retained in the process solids. No difference in the emissions of these metals was noted when portion of the coal was replaced by hazardous waste fuel.

2.9 Leaching test

There are a variety of tests available for characterizing the leaching behavior. These tests include agitated extraction tests, serial batch tests, flow-through tests, flow-around tests, etc. The leaching methods are separated into 3 types: (1) regulatory method are those approved by a regulatory agency to generate specific information for submission in a legal context (i.e. Toxicity characteristic leaching procedure (TCLP), Multiple extraction procedure (MEP), etc.); (2) standard methods are those adopted

by a standards organization (ASTM, ISO) for a specific set of conditions and sometimes for specific materials (i.e. Standard test method for single batch extraction method for wastes (ASTM method D-5233), Availability leaching test (NEN 7341), etc.); and (3) research methods developed for a particular objective. Regulatory and standard methods are frequently used for research projects. The leaching testing techniques that are widely used to evaluate the leaching amount of heavy metals from the cement include TCLP, Availability Test (NEN 7341), pH static leach test, and Notification of Ministry of Industry No.6 B.E. 2540 (1997). The detail of each method is described as follow:

2.9.1 Toxicity characteristic leaching procedure (TCLP) (U.S. EPA method 1311)

TCLP was developed in 1984 under the Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA). The method is the U.S. EPA regulatory method for classifying wastes as hazardous or non-hazardous based on toxicity. If the TCLP extract contains any one of the toxicity characteristic constituents in an amount equal to or greater than the concentrations specified in 40 CFR 261.24, the waste possesses the characteristics of toxicity and is a hazardous waste.

TCLP is designed to simulate the leaching of a waste if disposed in an unlined sanitary landfill. The method is an agitated extraction test using leaching fluid that is a function of the alkalinity of the solid phase of the waste. The TCLP is designed to determine the mobility of 40 toxicity characteristic constituents in liquid, solid, and multiphase wastes. The toxicity characteristic constituents include both inorganic and organic species. There is another test similar to the toxicity characteristic leaching procedure (TCLP) that describe by Ministry of Industry of Thailand.

2.9.2 Notification of Ministry of Industry No. 6 B.E. 2540 (1997)

According to the Notification of Ministry of Industry No.6, B.E. 2540 (1997), issued under Factory Act, B.E. 2539 (1996), stabilized and solidified materials must be tested for the leachate characteristics by leachate extraction procedure and

determined the concentrations of contaminants in extraction fluid. This test is similar to the toxicity characteristic leaching procedure (TCLP) to determine whether a waste exhibits hazardous characteristics based on the U.S. EPA Toxicity Characteristic (TC) criteria (40 CFR 261.24). Like the TCLP test method, leachate extraction procedure described in the Notification No.6 (1997). The extraction fluid made with 80% of sulfuric acid and 20% of nitric acid in deionized (DI) water to a pH of 5.0 is selected to mimic conditions in a acid rain. This test is applied to determine the leachate from the cement based-product, cement based-stabilized, and other materials.

Many previous researches studied the use of leaching test on cement-based products, cement-base stabilized and other materials. The TCLP is also used to investigate the leachability of heavy metals. Wang et al. (2000) investigated the leachability of chromium (VI) from solidification chromium (VI) with cement. The toxicity characteristic leaching procedure (TCLP) was used to observe the leachability of chromium (VI). The results concluded that the leachability of chromium (VI) during TCLP testing was dependent on the initial concentration and the time. They also concluded that the K_2CrO_4 /cement ratio should not be higher than 0.2% in order not to exceed the chromium concentration of 5 ppm established by the TCLP limit.

Wang and Vipulanandan (1996) also used extended TCLP to evaluate leached lead from cement-coal fly ash stabilized products. They found that addition of fly ash reduced the concentration of leached lead by 10% to 30% compared to only cement paste. However, as initial concentration of lead was greater than 10%, leached concentration of lead from all of stabilized products exceeded the regulatory limit.

Rachakornkij (2000) found that concentration of leached lead from raw Municipal solid waste incinerator fly ash failed to meet the TCLP limits. However, after stabilized in cement mortars, concentrations of all regulated metals passed the test.

Asavapisit and Chotklang (2004) investigated the potential utilization of alkali-activated pulverized fuel ash as a solidification binder to treat electroplating sludge. Compressive strength and leachability of heavy metals from the solidified

electroplating sludge were determined to assess the potential for utilization. Metals leaching from the solidified wastes were assessed using the toxicity characteristic leaching procedure (TCLP). The results showed that lead, cadmium and copper were not found in the toxicity characteristic leaching procedure leachates. Chromium, zinc and ferric were detected. In some cases, chromium exceeded U.S. EPA allowable limits.

2.9.3 Availability leaching Test (NEN 7341) (Netherlands Normalization Institute 1993)

The availability leaching test is an agitated extraction method that was developed in The Netherlands. It is based on leaching a finely ground sample under two controlled pH conditions. The purpose of the test is to indicate the quantity of an element that may be leached from a material under extreme environmental conditions, e.g. in the very long term, after disintegration of the material, when the material is fully oxidized, or with complete loss of acid neutralization capacity (de Groot and Hoede, 1994; Bradley et al, 2000).

The recent studies have used this method on cement-based products, cement-based stabilized and other materials. These leaching tests are also used to investigate the maximum leachability. Crannell et al., 2000 studied the heavy metal stabilization in municipal solid waste combustion ash using soluble phosphate. Reductions in leaching observed through the Dutch total availability leaching tests demonstrate the effectiveness of soluble phosphate in stabilizing lead, copper, zinc and cadmium in bottom ash. Availability leaching showed the reduction in the fractions available for leaching, which were 14% for cadmium, 98% for copper, 99% for lead and 36% for zinc.

Hohberg et al. (2000) investigated the development of a leaching standard for the determination of the environmental quality of concrete. The test protocol includes an availability test. The result from the availability test indicated that the precision in terms of repeatability of the test is good and the reproducibility is acceptable.

2.9.4 pH static leach test (CEN TC 292, The Netherlands)

The pH static leach test is now standardized in Working Group 6 of CEN TC 292 Characterization of Waste (van der Sloot et al, 2000). This method is an extraction of granular material at controlled pH. The purpose of the test is to determine the effect of decreasing or increasing pH conditions on leachability. Since the conditions are very different for different uses, the pH is one of the most crucial parameters governing the release of constituents from the solid phase into solution. This method is used to cover important differences in pH environment (van der Sloot et al, 2001; van der Sloot, 2002). Many previous researches studied the use of leaching tests on cement-based products, cement-base stabilized and other materials. These leaching tests are also used to investigate the leachability of heavy metals.

H.A. van der Sloot (2002) studied the characterization of the leaching behavior of concrete mortars and of cement-stabilized wastes with different waste loadings for long-term environmental assessment. The results from pH-dependent measurements on standard mortars and cement-stabilized waste showed that the chemistry has many similarities and some very pronounced chemical differences. Changes in the chemical environment, as they may occur in the long term, are addressed in the pH dependent tests by allowing an assessment of the magnitude and direction of change in leachability upon changes in external exposure conditions.

Bradley S. Crannell et al., 2000 studied the heavy metal stabilization in municipal solid waste combustion ash using soluble phosphate. Reductions in leaching observed through pH dependent leaching tests demonstrate the effectiveness of soluble phosphate in stabilizing lead, copper, zinc and cadmium in bottom ash. pH-dependent leaching showed that the treatment was able to reduce equilibrium concentrations by 0.5 to 3 log units for these heavy metals.

In summary, the conditions that were taken from literature review included the clinker burning duration from 30 minutes to 90 minutes and the burning temperature during 1400 - 1500°C (Kakali et al., 1997; Stephan et al., 1999; Trezza and Scian, 2000; Ract et al., 2003).